Indian J. Phys., **51B**, 50-57 (1977)

Polarised raman and infrared spectra of single crystals of p-chlorobromobenzene

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Single crystals of p-chlorobromobenzene were grown by using the zone refining technique. Twelve polarized Raman spectra of p-chloro bromo benzene single crystal have been recorded in intermolecular region and eight intermolecular region at different orientations of the crystal. Also six polarized infrared spectra have been recorded in the region 4000-250 cm^{-1}. The interpretation of the intramolecular and lattice vibrational modes have been made on the basis of intensities observed along different orientation of the crystal plates and the crystal structure (C^5_{2h}), assuming oriented gas model approximation.

1. INTRODUCTION

The near ultraviolet electronic absorption spectrum of p-chlorobromobenzene in vapour phase has been studied by Krishnamachari[1] and Srinivasacharya and Santhamma[2] and Raman active frequencies and their relative intensities have been reported by Kohlrausch *et al*[3,4] and Pausen[5]. Stojilikovic and Whiffen[6] have recorded the infrared spectra of all asymmetrical p-dihalogenobenzenes in CCl_4 solution and by KBr disc method. They have assigned the frequencies observed in the infrared spectra including those reported by earlier workers[3-5]. Polarized Raman and infrared spectra of single crystals of p-dichloro, p-dibromo and p-diiodobenzenes have been studied by several workers[7,8]. However, vibrational spectra of p-chlorobromobenzene single crystals have not been reported so far. In this paper polarized Raman and infrared spectra of p-chlorobromobenzene single crystals and the assignments of the observed intra and intermolecular frequencies are presented.

2. EXPERIMENTAL

Single crystals of p-chloro bromo benzene were grown by zone-refining technique, using multi-heating and single-heating, zone-refining units that have been fabricated in our laboratory[9]. The Raman spectra along different axes of the crystal (a cube of 1 cm edge length of a good quality crystal) using

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different polarizations of the incident and scattered radiation were recorded on a spectrophotometer equipped with Spex 1400-II double monochromator, Spectra-Physics 125 mW He-Ne laser, Spex cryostat fitted with ITT FW' 30-S-20 photomultiplier detector, Victoreen 1001 D.C. amplifier and a Texas Instrument recorder. 12 spectra were recorded at different incident and scattered polarization and propagation directions for the intramolecular modes and 8 were recorded for intermolecular (lattice) vibrations.

The polarized infrared spectra were recorded at room temperature on a Perkin-Elmer-521 infrared spectrometer in the region 4000-250 cm $^{-1}$. For each crystallographic axis, two polarized spectra were recorded with electric vector of the incident beam parallel and perpendicular to the crystallographic axis. In this six polarized infrared spectra were recorded. The accuracy of the measurement is estimated to be within 2 cm $^{-1}$. Typical Raman and infrared shown in figures 1 and 2.

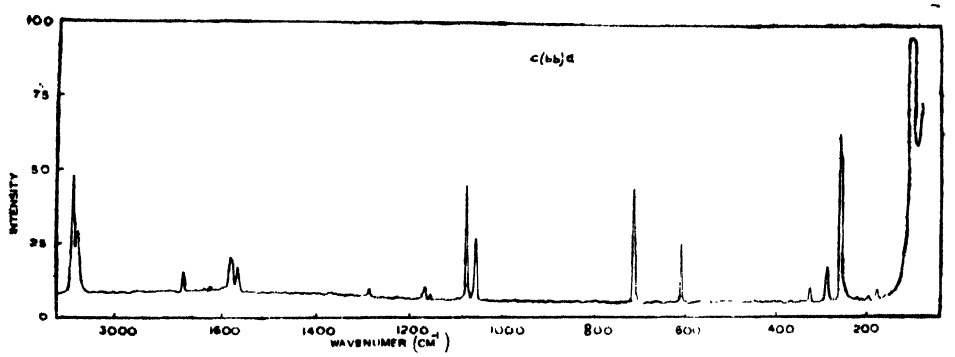

Fig. 1. Polarized Raman sectrum of b-chlorobromozenzene single crystal.

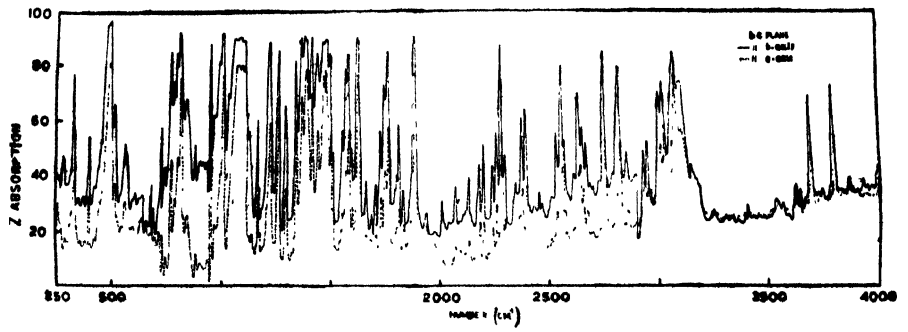

Fig. 2. Polarized infrared spectra of p-chlorobromobenze single srystal.

3. Crystal Structure

p-chlorobromobenzene crystal belongs to the monoclinic class having space group C^6_{2h} ($P_{2\,1/a}$) with two molecules per unit cell[10,11]. It is isostructural with p-dibromobenzene and p-dichlorobenzene crystals. The

unit cell parameters are : a = 15.2 Å, b = 5.86 Å, c = 4.11Å and β = 113°. Hendricks[10] has suggested that the symmetry of the crystal might be statistical, the halogen positions in molecules composing the structure being filled at random by bromine or chlorine or perhaps the two possible orientations of any given molecule differing by 180°, ae equally probable.

4. Results and Discussion

In free molecular state, p-chlorobromobenzene belongs to C_{2v} point group; the x-axis is taken perpendicular to the ring and the z-axis as that passing through the halogen atoms. The 30 normal modes of vibration of the free molecule are divided into :

$$11a_1 + 10b_2 + 3a_2 + 6b_1$$

All the frequencies are allowed in the Raman spectrum and all but the three belonging to a_2 species are allowed in infrared spectrum. However, in the crystalline state vibrations belonging to a_2 species also become infraredactive because of the fact that these vibrations are allowed both in site and factor group symmetries. The polarized Raman and infrared spectra of p-chlorobromobenzene crystals have been interpreted assuming the oriented gas model approximation.

A large number of bands (nearly 250) have been observed in single crystal infrared spectra; much greater than those observed in liquid, solution or vapour state. The bands appear usually in groups of three close-lying bands separated by ~ 3-6 cm^{-1} from the middle one, which is most intense and is usually the real fundamental frequency. The other two accompanying satellites are probably due to lattice vibrations. The appearance of additional bands in the crystalline state may be due to (i) combinations of fundamental frequencies with lattice vibrations; (ii) appearance of normally unallowed vibrational frequencies in crystalline state; (iii) sharpness of bands in crystalline state which considerably reduces the broad envelopes of strong bands observed in the liquid or solution phase. Doublet splittings due to crystal-field effect have also been observed in few cases and are found to be of the order of 2-6 cm^{-1}.

The intramolecular vibrations may be divided into two parts (i) phenyl ring vibrations and (ii) vibrations involving Cl and Br substituents.

Phenyl ring vibrations : Presence of aromatic ring structure in organic compounds is easily detected by a number of bands appearing in the region 1350-1600 cm^{-1}. These are due to C=C stretching modes. In single ring compounds there appear six frequencies belonging to $(3a_1 + 3b_2)$ species. Five of these have magnitudes lying in the region 1350-1600 cm^{-1}, while the sixth has a much lower magnitude. This lower frequency (ring breathing)

is observed at 1088 cm $^{-1}$ and 1089 cm^{-1} in Raman and infrared spectra respectively corresponding to 992 cm^{-1} (a_{1g}) frequency of benzene. Other C=C stretching frequencies have been observed at 1378, 1410, 1463, 1552 and 1572 cm^{-1} in infrared spectra and 1372, 1558 and 1570 cm^{-1} in Raman spectra.

The four C-H stretching frequencies are : 3050, 3060, 3068 and 3078 cm^{-1} observed in the infrared spectra and 3053, 3060, 3068 and 3075 cm $^{-1}$ observed in the Raman spectra.

The 606 cm^{-1} (e_{2g}) vibration of benzene (C-C-C in-plane-bending) splits up into two components on substitution. One component is lowered while the other retain nearly the same value. Frequencies 489 and 656 cm^{-1} observed in infrared spectra and 651 cm^{-1} in Raman spectra are assigned to this mode. The other C-C-C in-plane bending frequency is observed at 1006 cm^{-1} and corresponds to b_{1u} (1010 cm^{-1}) mode of benzene.

Similar to the planar bending modes the frequencies 263, 400 and 695 cm $^{-1}$ observed in the infrared spectra and 261 and 690 cm $^{-1}$ observed in Raman spectra have been assigned to C-C-C out-of-plane bending modes corresponding to e_{2u} and b_{2g} modes of benzene.

The frequencies 1290, 1172, 1167 and 1070 cm $^{-1}$ observed in infrared spectra supported by 1294, 1174, 1167 and 1069 cm $^{-1}$ Raman frequencies have been assigned to C-H in-plane bending modes. Similarly 770, 810, 950 and 992 cm^{-1} vibrations observed in infrared spectra are assigned as C-H out-of-plane bending modes. However, in the Raman spectra only 812 cm^{-1} frequency is observed in this region.

Substituent group vibrations : On account of the substitution of the two atoms (Cl and Br) in benzene ring, six C-substituent vibrations are expected. The C-Cl stretching, in-plane bending and out-of-plane bending vibrations have been observed at 730, 472 and 330 cm $^{-1}$ respectively in infrared spectra. In Raman spectra C-Cl stretching and out of plane bending frequencies 729 and 332 cm^{-1} are observed. The frequencies 624, 290 and 180 cm^{-1} observed in Raman spectra and 624 and 288 cm^{-1} observed in infrared spectra* have been assigned to C-Br stretching, in-plane bending and out-of-plane bending modes respectively. It is seen that C-Cl vibrations are stronger in intensity than the corresponding C-Br vibrations in both Raman and infrared spectra.

The observed Raman and infrared fundamental frequencies are presented in tables 1 and 2.

* infrared spectra below 250 cm^{-1} could not be recorded on Perkin-Elmer-521 spectrometer.

Table 1. Intramolecular frequencies and their assignments of p-bromochloro-benzene single crystal

Raman shift cm^{-1}	b(ab)c	b(cb)c	b(aa)c	b(ca)c	b(cc)a	c(ac)a	c(bc)a	c(ac)a	c(ab)a	c(bb)a	b(cb)a	b(ab)a	Assignments
180	5	18	5	10	14	19	—	—	12	13	—	9	C-Br op. bending
261	65	89	75	75	38	90	42	46	100	80	31	37	C-C-C op. bending
290	15		22	43	48	89	31	24	31	30	38	20	C-Br ip. bending
332	6	19	10	13	9	13	7	7	15	16	6	9	C-Cl op. bending
624	22	41	39	33	18	42	19	—	44	37	16	24	C-Br stretching
651	—	—	—	—	—	—	—	17	—	—	—	—	C-C-C i.p. bending
690	—	—	—	9	8	—	—	—	—	—	—	—	C-C-C o.p. bending
729	43	80	100	62	64	74	34	37	87	64	29	33	C-Cl stretching
812	—	—	—	8	9	6	—	—	7	—	—	—	C-H o.p. bending
1069	23	48	33	26	6	26	21	20	32	24	19	18	C-H i.p. bending
1088	44	79	58	43	50	46	36	37	56	40	34	32	C-C strenching (Ring breathing)
1167	3	—	5	—	—	—	—	—	—	—	—	—	C-H i.p. bending
1174	6	25	9	10	10	9	9	9	11	8	6	6	C-H i.p. bending
1294	5	18	4	5	—	4	6	—	6	5	—	6	C-H i.p. bending
1372	—	—	3	—	5	—	—	—	—	—	—	—	C=C stretching
1588	13	32	10	6	7	7	10	12	7	5	10	9	C=C stretching
1570	17	42	7	8	7	9	13	14	11	6	11	14	C=C stretching
3053	26	46	20	7	4	10	24	20	8	—	26	26	C=C stretching
3060	47	—	40	14	11	16	46	47	17	7	42	36	C=H stretching
3068	—	10	—	—	—	—	—	—	—	13	—	—	13=H stretching
3075	—	—	—		15	—	—	—	—	—	—	—	C-H stretching

i.p. = in plane
o.p. = out of plane

Table 2. Polarized infrared spectra p-chlorobromobenzene single crystal (fundamental frequencies)

Frequencies cm^{-1}	Relative intensity						Assignments
	ab plane		ac plane		bc plane		
	∥ to a axis	∥ to b axis	∥ to a axis	⊥ to c axis	∥ to axis	⊥ to c axis	
263	24	25	45	45	—	18	C-C-C out of plane bending
288	14	34	55	46	33	15	C-Br in plane bending
330	68	74	59	49	67	70	C-Cl out of plane bending
400	32	43	55	35	50	14	C-C-C out of plane bending
472	73	78	96	96	100	—	C-Cl in plane bending
489	100	96	100	92	100	100	C-C-C in plane bending
624	—	—	15	—	5	—	C-Br stretching
656	30	9	42	78	57	11	C-C-C in plane bending
695	26	15	41	64	58	17	C-C-C out of plane bending
730	65	53	56	61	74	45	C-Cl stretching
770	98	91	85	74	86	92	C-H o.p bending
810	87	99	97	95	90	91	C-H o.p bending
950	78	94	93	92	88	97	C-H o.p. bending
992	88	85	87	60	77	87	C-H o.p bending
1006	99	100	100	93	86	97	C-C-C in plane bending
1070	99	98	100	94	—	96	C-H in plane bending
1089	100	97	99	100	92	96	C - C stretching
1167	57	57	27	55	59	64	C-H in plane bending
1172	30	27	23	—	61	44	C-H in plane bending
1290	64	63	42	58	64	60	C-H in plane bending
1378	100	98	83	93	84	96	C=C stretching
1410	99	97	82	87	84	95	C—C stretching
1463	100	97	—	94	84	97	C=C stretching
1552	53	52	35	40	59	49	C=C stretching
3050	—	47	49	45	65	—	C-H stretching
3060	75	—	63	54	69	63	C-H stretching
3068	79	86	—	—	—	—	C-H stretching
3078	100	90	76	77	85	97	C-H stretching

In the Raman spectra factor group splitting have been observed in two C=C stretching frequencies : 1558 and 1570 cm^{-1}; with components at 1557 and 1559 cm^{-1} and 1568 and 1572 cm^{-1} respectively. This is explained as carbon-carbon interaction in the unit cell. The crystal structure suggests that carbon-carbon interaction with two molecules per unit cell is appreciable due to the two carbon atoms being rather close,

In the infrared spectra doublet splittings of 4 to 6 cm^{1-} have been observed in a number of frequencies and are presented in table 3.

Table 3

Frequency (mean value) cm^{-1}	Doublet components cm^{-1}	Proposed assignment
400	398, 402	C-C-C o.p bending
489	487, 491	C-C-C i.p. bending
810	808, 812	C-H o.p. bending
1006	1004,1010	C-C-C i.p. bending
1167	1165,1170	C-H i.p. bending
1463	1460,1465	C=C stretching

Lattice vibrations

The lattice vibrations are rotatory and translatory types which correspond to pure rotations and translations respectively respectively in the limit where the interaction between the molecules vanishes With n molecules per unit cell there are 6n-3 lattice vibrations. Lattice frequencies usually fall in far infrared region and appear close to the exciting line in the Raman spectrum of crystals In primitive cell of p-chlorobromobenzene crystal containing two molecules per unit cell, there are 9 lattice vibrations: of which rotational lattics modes (a_g, b_g) are active and the translational modes (a_u, b_u) are forbidden in the Raman spectrum but translational modes are allowed in the infrared spectrum. Vuks[12] has observed 20, 37 8 and 93 cm^{-1} frequencies in the Raman spectrum of p-chlorobromobenzene crystal and has explained their occurrence on the assumption that the lines originate in the rotational oscillations of the molecules in the lattice.

In the present case six lattice frequencies have been observed in the Raman spectrum : 13, 23, 46, 77, 97 and 113 cm^{-1}. In view of the Factor group C_{2h}, out of the six Raman active frequencies, three would belong to a_g species and three to b_g species. The frequencies 23, 77 and 97 cm^{-1}

present in aa, bb, cc and ac polarisation belong to a_g mode and the frequencies 13, 46 and 113 cm^{-1} present in ab and bc polarisations belong to b_g modes. These frequencies have also been observed in a number of combination and difference bands appearing in the infrared absorption spectrum of p-chlorobromobenzene crystals.

ACKNOWLEDGMENTS

One of the authors (Shyampati) is grateful to C S I R., New Delhi for providing financial assistance.

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* Only abstract available to authors.